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(54) Subject of Invention

Manufacturing Method of Quartz Glass Preform for Optical

Transmission

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DETAILED DESCRIPTION

1. Subject of Invention

Manufacturing method of quartz glass preform for optical transmission

2. Scope of the Patent Application

1. A manufacturing method of quartz glass preform having the following characteristics: An ester silane expressed by the general equation

$R^1_n Si(OR^2)_{4-n}$ (where, R^1 is hydrogen atom, methyl or ethyl group; R^2 is methyl group or ethyl group; n is an integer number of 0 to 4), and dopants expressed by $Ge(OR^3)_4$ and/or $B(OR^3)_3$ (where R^3 is a univalent hydrocarbon group) and/or PH_3 are heat-combusted in a quartz tube and the generated silica containing the dopant(s) is layer-deposited as transparent glass film on the inside wall of the quartz tube. Then the quartz tube is heat-melted to consolidate the center (eliminate the hollow center).

3. Detailed Explanation of the Invention

The present invention is related to manufacturing methods of quartz glass preform for optical transmission, especially to the manufacturing method of quartz glass preform, for optical transmission, containing no chlorine in either elemental state or compound state by inside MCVAD method.

Relative to the manufacturing methods of quartz glass preform for optical transmission, various methods are known. In these methods, because the purity has to be extremely high and further the refractive index in the cross sectional direction

has to be controlled, chemical vapor deposition methods (CVD methods) utilizing chemical reaction are widely employed. And for these CVD methods, the followings are known: the inside deposition method (MCVD method) in which the obtained silica through oxidation of silicon compound is formed as transparent glass film inside a quartz tube; the outside deposition method in which the silica prepared by flame hydrolysis of silicon compound is deposited on the surface of a core material; and the vapor axial deposition method (VAD method) in which the silica prepared by flame hydrolysis of silicon compound is deposited on a rotating heat-resistant material to form a rod shape body. The outside deposition method and the VAD method are different from MCVD method in that since the reaction is not performed in a sealed system, the refractive index control of the preform is difficult. Hence for the manufacturing of high quality optical fiber, an inside deposition MCVD method, in which the amount of dopant can be easily controlled, is deemed to be preferable.

However, in the publicly known inside deposition MCVD method, from one end of the quartz tube, silicon tetrachloride $(SiCl_4)$ as the glass forming raw material and dopant(s) for controlling the refractive index, such as germanium tetrachloride $(GeCl_4)$, phosphorus oxychloride $(POCl_3)$, and boron trichloride (BCl_3), are introduced along with oxygen for carrying out oxidation. Meanwhile from the outside of the quartz tube, oxygen-hydrogen flame or an electric heating equipment is moved (traversed) from the gas supplying side to the gas exhausting side, repeatedly, to heat the gases

introduced. And by the vapor phase reaction, the formed dopant containing silica is deposited/accumulated as transparent glass film in the length direction of the quartz tube inside. Following this, the glass film layers containing, hollow quartz tube is consolidated to complete a quartz glass preform. Because of the above described procedures, in the quartz glass preform obtained by this method, a great deal of chlorine or chlorine compounds will be dissolved-included. By the presence of these dissolved chlorine/chloride, there will be an disadvantage that the adsorption loss will occur at visible region 0.6--1.1 um wavelength band. Additionally, the presence of the dissolved chlorine/chloride will cause problem in creating blisters during the consolidation or fiber drawing process.

Moreover, in this inside deposition MCVD method, as described above, the heat required for the vapor phase reactions of the raw materials to occur is provided from the outside of the quartz tube, and by the heating from the outside, the quartz glass tube is heated to the softening point. Because of these procedures, formations of twisting or bending to the quartz tube can easily occur. And when the glass deposited layer becomes thicker, the heat conduction will become poorer and this will accordingly require an increase in the heating from the outside. As a result, the deformation will be accentuated. In addition, particularly, when an oxygen-hydrogen flame is employed as the outside heating sauce, in order to increase the heating temperature, the hydrogen has to be increased and by this, the

flame speed will increase. As a result, there will be a tendency to easily accelerate the deformation. Further, this deformation will make the thickness of the glass deposited layer heterogeneous, and the intended refractive index distribution will be drastically disturbed. This disadvantage often accompanied the deformation.

The present invention is related to the manufacturing method of quartz glass preform for optical transmission by the inside deposition MCVD method in which the above mentioned disadvantage is resolved. The method is characteristically as follows. An ester silane expressed by the general equation $R^1_n Si(OR^2)_{4-n}$ (where, R^1 is hydrogen atom, methyl or ethyl group; R^2 is methyl group or ethyl group; n is an integer number of 0--4) and dopants expressed by $Ge(OR^3)_4$ and/or $B(OR^3)_3$ (where R^3 is a univalent hydrocarbon group) and/or PH_3 are heat-combusted in a quartz tube, and the generated silica containing the dopant(s) is layer-deposited as transparent glass film on the inside wall of the quartz tube. Then the quartz tube is heat-melted to consolidate the center (eliminate the hollow center).

To explain further, the present inventors carried out investigations on the manufacturing method of quartz glass preform for optical transmission, especially for (the purpose of) achieving no inclusion of halogen atom or halogen compounds and for achieving the desired refractive index distribution. The studies were focused on the fact that the uses of silanes (silane compounds) and dopants, which contain no halogen or

halogen compounds in their molecules, as the glass forming raw material and dopant, could achieve the objective. For the silanes, if the ester silanes shown by the aforementioned general equation are employed, the boiling point would be roughly higher than $100^{\circ}C$; the combustion rate would be small; the handling would be easy; and the price would be low in industrial scale. Further for the dopants, if the alcoxy group containing germanium and boron and/or PH_3 are employed, they would not contain halogen atoms, and their reaction efficiencies at low temperature would be high. Therefore, by using these raw material gases and dopants, definitely a quartz glass preform, which contains no halogen atom or halogen compounds and possesses excellent refractive index distribution can be obtained. Additionally, in using these, the reaction efficiency difference by the gas types will disappear. Furthermore, these gases are easier to react compared to the conventional ones; thus the heat quantity required for the heating from the outside of the quartz tube will be small. For example, when oxygen-hydrogen flame is employed as the outside heating source, the hydrogen amount for the heating can be cut down to 1/5 to 1/2 that of the conventional approach to make the flame weaker. As a result, the deformation of the quartz tube can be prevented and it was discovered that the goal of excellent refractive index distribution of the quartz glass preform can be achieved. In view of this, the various conditions were further investigated to complete the present invention.

In the method of the present invention, as described above,

the ester silane to be used as glass forming raw material can be expressed by general equation $R^1_nSi(OR^2)_{4-n}$. For example, methyltrimethoxysilane, dimethyldimethoxysilane, trimethylmethoxysilane, tetramethoysilane, methyltriethoxysilane, tetraethoxysilane, etc. can be listed. From the standpoints of inexpensive price and easier handling, industrially, methyltrimethoxysilane and tetramethoxysilane are preferable.

These ester silanes can be easily obtained by reacting trimethylchlorosilane and methyltrichlorosilane with alcohol such as methanol and ethanol; the former two are by-products generated in the dimethyldichlorosilane synthesis from the direct reaction of methyl chloride and metallic silicon to produce the main raw materials for silicone rubber, silicone varnish and silicone oil. They also can easily obtained by reacting the mixture of monomethyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane and monomethyldichlorosilane with alcohols; the above mixture is obtained by thermal decomposition of polymethylpolychloropolysilane and polymethylpolychloropolysiloxane expressible by general equation $(CH_3)_nSimCl_xO_y$, obtainable in the dimethyldichlorosilane manufacturing process. The tetramethoxysilane can be manufactured by reacting metallic silicon and methyl alcohol in the presence of $NaOCH_3$ as catalyst according to the equation below:

$$Si + 4\ CH_3OH \xrightarrow[100\text{--}110^{o}C]{NaOCH_3} Si(OCH_3)_4 + 2\ H_2$$
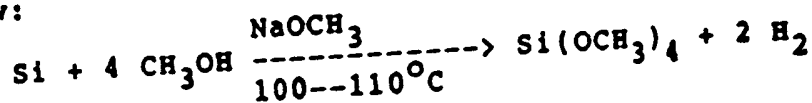
Therefore, it can be cheaply supplied industrially. Additionally, through distillations of the raw materials, chlorosilane or its ester silane, high purity materials containing no impurities can be obtained. Thus the advantage is that by using these high purity materials, high purity quartz glass preform can be obtained.

Meanwhile the dopants to be used in the method of the present invention can be expressed by the aforementioned formulas: $Ge(OR^3)_4$, $B(OR^3)_3$ and PH_3. For example, $Ge(OCH_3)_4$ (boiling point 150°C), $Ge(OC_3H_5)_4$ (boiling point 190°C), $Ge(O-n-C_3H_7)_4$ (boiling point 240°C), $Ge(O-n-C_4H_9)_4$ (boiling point 290°C), $B(OCH_3)_3$ (boiling point 68°C), $B(OC_2H_5)_3$ (boiling point 117°C), $B(O-n-C_3H_7)_3$ (boiling point 176°C), and $B(O-n-C_4H_9)_3$ (boiling point 227°C) can be listed. Among them, the ones with R^3 group in either methyl group or ethyl group are relatively low in boiling point and can be supplied into the reaction chamber along with a carrier gas; thus they are preferable. Further, the manufacturing method of these $Ge(OR^3)_4$ and $B(OR^3)_3$ are publicly known. For instance, they can be easily obtained by the methods described in J. Amer. Chem. Soc., 1953, 75, p. 718; J. Chem. Soc., 1956, p. 4916; Encyclopedia of Chemical Technology 3rd Ed. Vol. 4, p. 111, etc. Relative to the PH_3 (boiling point -88°C), this a typical compound among the phosphorous compounds which contain no halogen. It exhibits extremely high combustion efficiency either in air or oxygen. High purity grade can be obtained in cylinder-filled form. Because of these reasons, it is considered to be most suitable.

In the method of the present invention, the mixed gas of ester silane and the dopant is transported, with carrier gas if necessary, and introduced into a quartz tube along with oxygen gas as oxidizing agent to carry out oxidation reaction in the quartz tube, and the generated silica containing the dopant is deposited onto the inside wall of the quartz tube. Furthermore, in the conventional publicly known inside deposition MCVD method, for homogeneously depositing the silica generated from the transported reactant gases fed into the quartz tube on the inside wall of quartz tube, the oxygen-hydrogen flame burner is successively moved along the quartz tube, and (repeated) back and forth movements have to be performed. However, in the present invention, both the ester silane and the dopant are combustible material and they will be combusted immediately at the tip of the feed-nozzle used for introducing the gas to become silica containing dopant and deposited on the quartz tube wall. Therefore in practice, it is preferable that the heating source such as oxygen-hydrogen flame burner is fixed and the quartz tube itself is moved to carry out the back and forth movements. And if the transporting speed of the raw material gases into the quartz tube is too small, there is a worry of back fire phenomenon to accompany the process. Therefore, it is better to spray them into the quartz tube inside with sufficient flow rate. Also if the oxygen gas is not mixed in the raw material gasses, the combustion speed will be lowered and there will be a concern for not achieving complete combustion. Thus it is desirable to mix the oxygen immediately before the

feed-nozzle.

Furthermore, the silica deposited on inside of the quartz tube will be melted by the gas combustion heat, and by the burner or electric heating from outside to become a glass film coating on the inside wall of the quartz tube. This silica or the glass film contains dopant, and by the amounts of the dopant, different refractive indexes will be exhibited. Therefore, in practice, it is better to successively vary the dopant concentration in the raw material mixed gas so that glass films having the successively specified refractive indexes in the inside-diameter direction of the quartz tube will be successively deposited.

And the obtained quartz tube with dopant containing glass layers deposited on its inside wall is then heat-melted for consolidation to become quartz glass preform. To carry out this, the conventional publicly known collapsing process can be suitably applied. For example, the method below can be adopted: the quartz tube is heat-melted at about 2,000°C and the viscosity of the malted glass and the surface tension of the glass are utilized to achieve solidification collapsing so that no air will remain inside.

Next, the present invention is illustrated based on the attached figures. Fig 1 is the cross section diagram of the equipment for performing the present invention method. Fig 2 is the cross section diagram showing the movement of the quartz tube. The raw material gas and dopants, contained in ester silane container 1, $Ge(OR^3)_4$ container 2, $B(OR^3)_3$ container 3

PH_3 container 4, are each transported by the argon gas introduced from tube 5, as carrier gas, into mixing vessel 6, mixed together with the oxygen transported from introduction tube 7, and then introduced into quartz glass tube 8. The introduction of this gas mixture is conducted by spraying into inside of the quartz tube from the feed-nozzle 9; however, since the quartz tube 8 is being heated from outside by oxygen-hydrogen burner 10, the gas introduced here will be combusted at the tip of feed-nozzle 9. By this oxidation reaction, the gas will become dopant containing silica and the silica will be deposited inside-wall of the quartz tube being rotated. Since the quartz tube is successively moved from one end to the other against the stationary burner, the silica will deposited uniformly on the inside-wall of quartz tube. And the silica will be melted by the raw material gas combustion heat and the heating by the burner to become glass layers accumulated on the quartz tube wall. Portions of the silica, which have not been converted to glass film, and the exhaust gas are exhausted to outside from the other end of the quartz tube. Fig 2 shows the movement of the quartz tube. It is shown that the quartz tube 8 will move such as from Fig a) to Fig b) position against the fixed burner 10. It indicates that after it moves to the end as shown in Fig b), it will immediately reverted to Fig a) position; this procedure is used to successively form glass films.

In this case, the doped amounts of the dopant against the ester silane are adjusted to either increase or decrease with

time so that the dopant concentrations contained in the glass films deposited on the quartz tube will show the predetermined refractive index. When the glass film reaches the specified thickness, the supply of the raw material gas is stopped and then the hollow quartz tube is consolidated by the aforementioned collapsing process to obtain the aimed quartz glass preform.

In essence, in the method of the present invention, ester silane and dopant containing no halogen atom or halogen compound are used as starting materials; and by inside deposition MCVD method, glass layers containing dopant(s) are accumulated and through melting consolidation, quartz glass preform for transmission is manufactured. By this approach entirely no halogens atom and halogen compounds will be contained. Therefore the quartz glass preform with no optical absorption loss by the presence of halogens can be easily obtained. Furthermore, due to the good reactivity of the dopants at low temperature, the variations in the refractive index distribution will be small and a quartz glass preform for optical transmission having large specific refractive index difference can be easily obtained. In this case, compared to the conventional method, the heating from the outside can be made lower in temperature to prevent deformation of the quartz tube. As a result, it provides an advantage in that a quartz glass preform having desirable refractive index distribution can be easily obtained.

Performance examples of the present invention are given

below.

Performance Example 1

A synthetic quartz tube, 30 mm in outside diameter and 1000 mm in length was employed and the equipment shown in Fig 1 was constructed. Methyltrimethoxysilane $[CH_3Si(OCH_3)_3]$, as raw material gas and $Ge(OC_2H_5)_4$ and PH_3, as dopant were employed. These materials were transported by argon, mixed with oxygen gas and supplied into the quartz tube through feeder-nozzle.

And the quartz tube was heated by an oxygen-hydrogen burner; the burner was fixed; and the quartz tube was moved with 150 mm/minute speed. During the 100 times moving-heating, the raw material gas, dopants and oxygen amounts were changed as shown in Fig 3 to form 100 layers of glass films composed of $SiO_2-P_2O_5-GeO_2$.

Then the supply of the raw material gas was stopped and the outside heating temperature was raised to consolidate the quartz tube to a rod shape quartz glass preform.

The obtained quartz glass preform was transparent. It was measured for the cross sectional refractive index distribution: the result indicated the graded index type as shown in Fig 4. The fiber prepared from this preform was analyzed using an x-ray micro-analyzer: chlorine atom was not detected. Also no blister forming occurred when the preform was pulled. The absorption loss originating from chlorine atom was entirely absent.

Performance Example 2

A synthetic quartz tube, 30 mm in outside diameter and 1000 mm in length was employed and the equipment shown in Fig 1 was

constructed. As raw material gas 100 c.c. (value per minute; same for values given below) of methyltrimethoxysilane and as dopants, 200 c.c. of $B(OCH_3)_3$ were transported using 400 c.c. of argon gas. To this mixture, 1,850 c.c. of oxygen gas were mixed and the mixture was introduced into the quartz tube. Similar treatment described in Performance Example 1 was applied to form 30 layers of $SiO_2-B_2O_3$ composition glass films on inside-wall of the quartz tube as clad layer.

Next, as raw material, 100 c.c. of methyltrimethoxysilane and as dopants, 10 c.c. of PH_3 and 30 c.c. of $Ge(OC_2H_5)_4$ were transported using 300 c.c. of argon gas. To this mixture, 1,250 c.c. of oxygen gas were mixed and the mixture was introduced into the quartz tube. Similar treatment described in Performance Example 1 was applied to form 70 layers of $SiO_2-P_2O_5-GeO_2$ composition glass films on the inside-wall of the quartz tube as core layer.

Then the supply of the raw material gas was stopped and the outside heating temperature was raised to consolidate the quartz tube to a rod shape quartz glass preform.

The obtained transparent glass body was measured for the cross sectional refractive index distribution; the result indicated the step index type as shown in Fig 5 a. The fiber prepared from this preform was analyzed using a x-ray micro-analyzer: chlorine atom was not detected. Also no blister forming occurred when the preform was pulled. The absorption loss originating from chlorine atom was entirely absent.

Performance Example 3

A synthetic quartz tube, 30 mm in outside diameter and 1000 mm in length was employed and the equipment shown in Fig 1 was constructed. As raw material 100 c.c. of tetramethoxysilane [$Si(OCH_3)_4$], and as dopant, 200 c.c. of $B(OC2H5)_3$ were transported using 200 c.c. of argon gas. To this mixture, 2,900 c.c. of oxygen gas were mixed and the mixture was introduced into the quartz tube. Similar treatment described in Performance Example 1 was applied to form 50 layers of SiO_2-B_2O_3 composition glass films on the inside-wall of the quartz tube as clad layer.

Next, as raw material, 100 c.c. of tetramethoxysilane and as dopant, 10 c.c. of PH_3 and 35 c.c. of $Ge(OCH_3)_4$ were transported using 300 c.c. of argon gas. To this mixture, 1,000 c.c. of oxygen gas were mixed and the mixture was introduced into the quartz tube. Similar treatment described in Performance Example 1 was applied to form 50 layers of SiO_2-P_2O_5-GeO_2 composition glass films on the inside-wall of the quartz tube as core layer.

Then the supply of the raw material gas was stopped and the outside heating temperature was raised to consolidate the quartz tube to a rod shape quartz glass preform.

The obtained transparent glass body was measured for the cross sectional refractive index distribution; the result indicated the step index type as shown in Fig 5 b. The fiber prepared from this preform was analyzed using a x-ray micro-analyzer: chlorine atom was not detected. Also no blister forming occurred when the preform was pulled. The absorption

loss originating from chlorine atom was entirely absent.

4. Brief Explanation of Figures

Fig 1 is the cross section outline diagram of the equipment for performing the method of the present invention. Fig 2 is the cross section diagram showing the movement of the quartz tube. Fig 3 is the graph showing the gas flow rates of raw material gas, dopants and oxygen gases. Fig 4 and Fig 5 a & b show the refractive index distribution diagrams of the quartz glass preforms prepared in Performance Example 1 and Performance Example 2 & 3, respectively.

1... Ester silane container

2... $Ge(OR^3)_4$ container

3... $B(OR^3)_3$ container

4... PH_3 container

5, 7... Introduction pipe   6... Mixing equipment

8... Quartz glass tube

9... Feed-nozzle (Note: both feed-nozzle and feeder-nozzle were used in the Japanese text: they are translated accordingly.)

10... Burner

Patent Applicant: Shinyetsu Kagaku Kogyo (Chemical Industries) K K
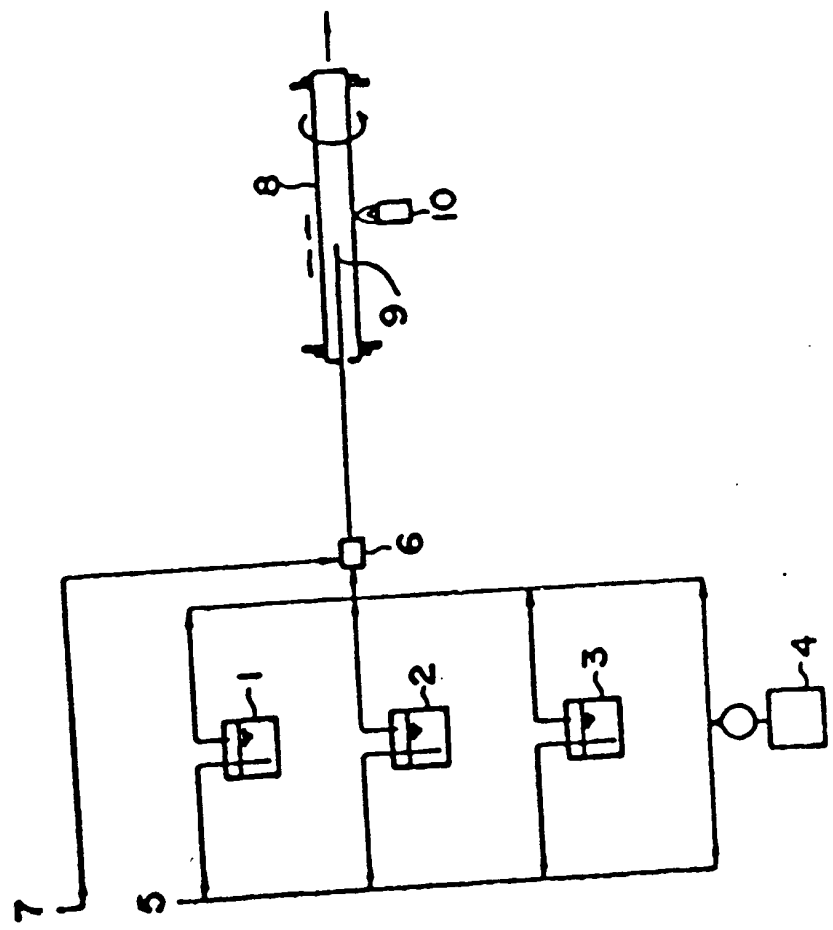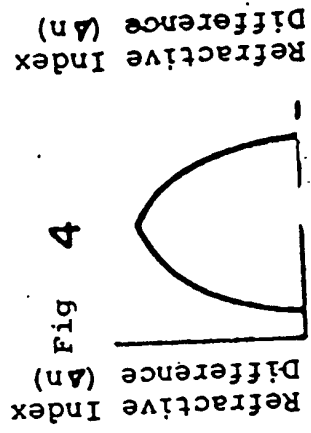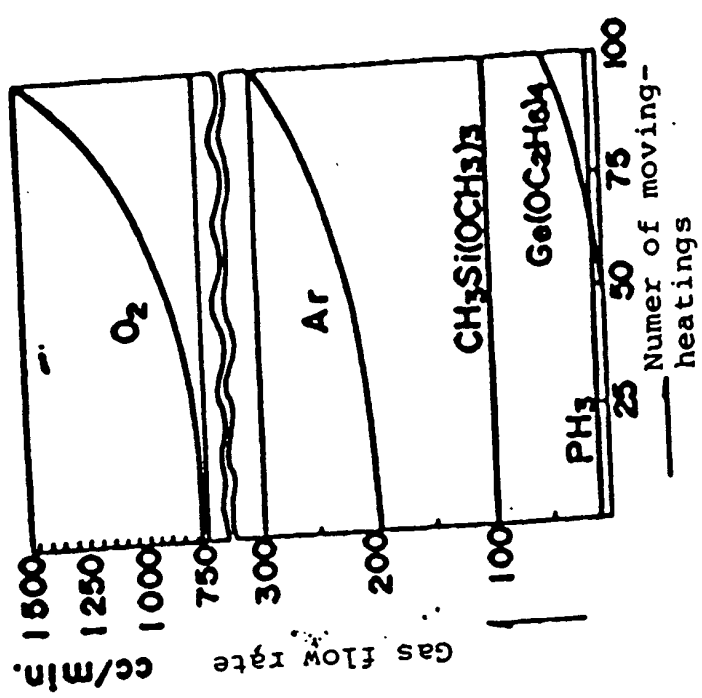
Agent , Attorney: Ryoichi Yamamoto

Fig 3

i

O₂

Ar

CH₃Si(OCH₃)₃

Ge(OC₂H₅)₄

PH₃

1500
1250
1000
750
300
200
100

cc/min.

Gas flow rate

Numer of moving-heatings

25 50 75 100

Fig 5

b
a

Refractive Index Difference (Δn)

Relative radius position (r)

Fig 4

Refractive Index Difference (Δn)

Relative radius position (r)

Fig 1

7

5
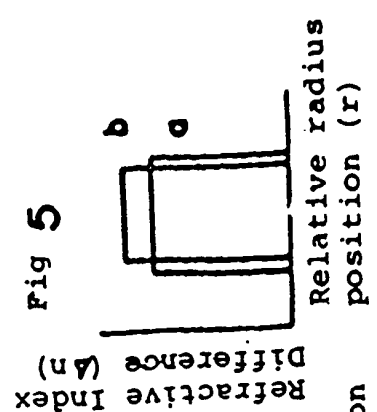
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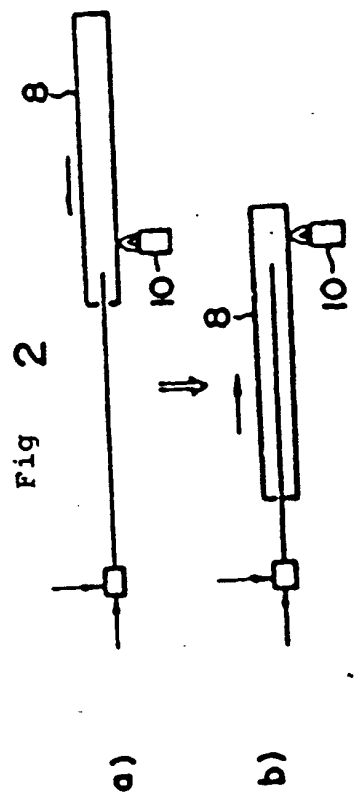3

4

6

8

9

10

Fig 2

8

10

8

10

8

10

a)

b)

Amendment Procedure

February 10, 1984

To: Patent Office Director   Mr. Kazuo Wakasugi

1. Case Identification

   Patent Application No. 198270-1983

2. Subject of Invention

   Manufacturing method of quartz glass preform for optical

   transmission

3. Amending Party

   Relation to the Case: Patent Applicant

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5. Date of Amendment Order

   Delivering Date: January 31, 1984

6 Object of Amendment

   Figures

7. Content of Amendment

   As shown in separate sheet